

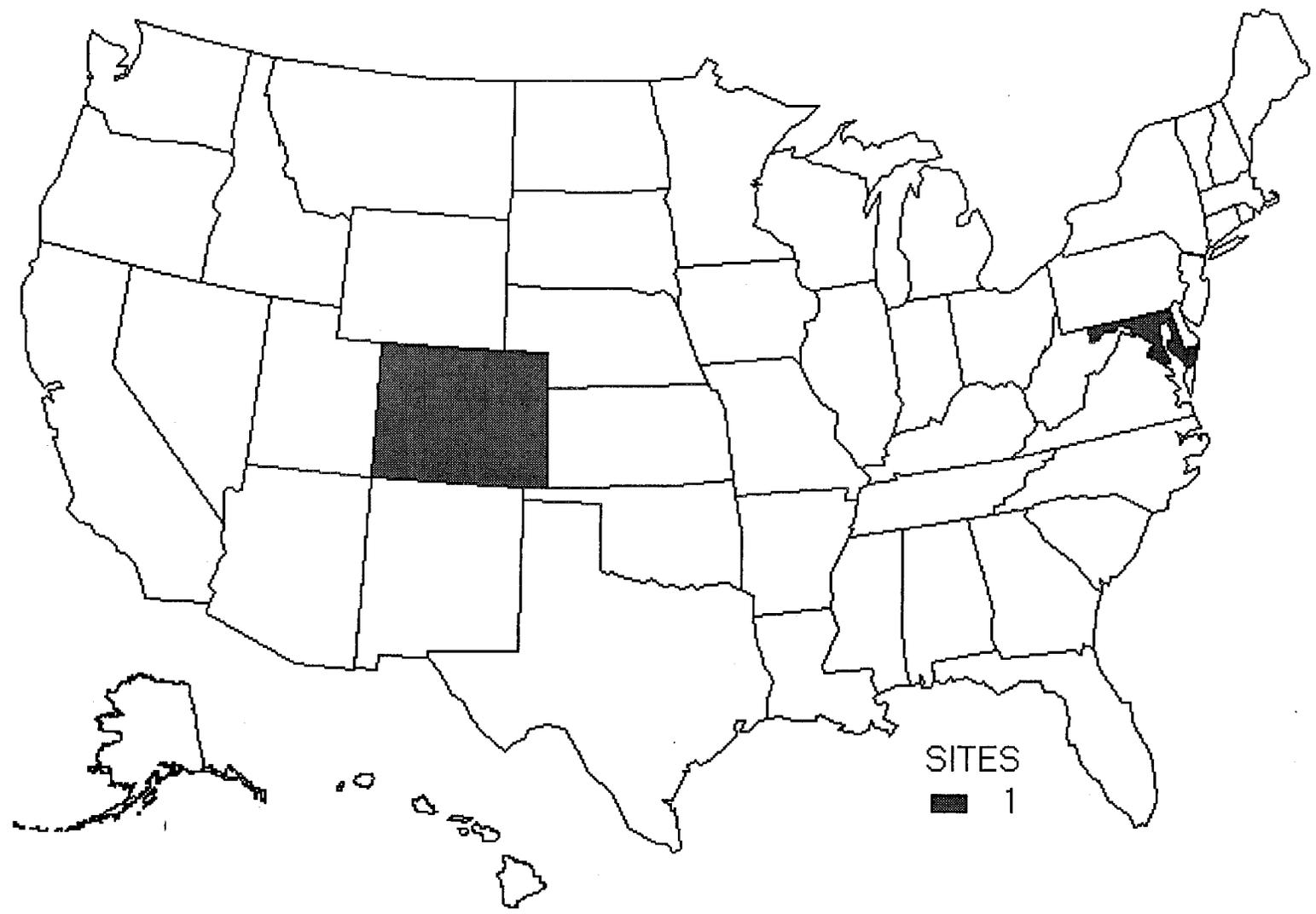
5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Diisopropyl methylphosphonate has been identified at 2 of the 1,416 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 1997). One site, identified in Figure 5-1, is the RMA located near Denver, Colorado. As diisopropyl methylphosphonate was never made commercially, the EPA neither expects nor routinely looks for this chemical at hazardous waste sites unless site history indicates it might be present.

Diisopropyl methylphosphonate was released at the RMA near Denver, Colorado, during 1953-1957 as a byproduct in the effluent from the manufacture of the nerve agent GB (Sarin). It is not a nerve gas and is not a metabolite or degradation product (Roberts et al. 1995). Contamination was confined primarily to the groundwater and, to a lesser extent, surface water and soil. Because of its low volatility, diisopropyl methylphosphonate is not likely to contaminate the atmosphere, and diisopropyl methylphosphonate does not undergo any significant photolysis (direct or indirect) in water. Biotransformation of diisopropyl methylphosphonate has not been detected in natural waters. Biotransformation of diisopropyl methylphosphonate is very slow in soil and is temperature dependent. Diisopropyl methylphosphonate is relatively mobile in soil. The presence of a nonreactive carbon-phosphorous (C-P) bond contributes to the environmental persistence of diisopropyl methylphosphonate. Bioconcentration has been demonstrated in plants, primarily in leaves. Consequently, it is possible that diisopropyl methylphosphonate may enter the food chain via animal feed. Exposure of the general population to diisopropyl methylphosphonate is expected to be low. If exposure does occur, it is most likely to arise from drinking or showering with diisopropyl methylphosphonate-contaminated water at or near the RMA, or through ingestion of fruits and vegetables that have been irrigated with such contaminated water.

Figure 5-1. Frequency of NPL Sites With Diisopropyl Methylphosphonate Contamination*



*Derived from HazDat 1998

5.2 RELEASES TO THE ENVIRONMENT

Releases of diisopropyl methylphosphonate are not required to be reported under SARA Section 313; consequently, there are no data for these compounds in the 1995 Toxics Release Inventory (TRI) (TRI95 1997).

5.2.1 Air

No specific information was found on the releases of diisopropyl methylphosphonate to air. However, diisopropyl methylphosphonate is unlikely to be an atmospheric contaminant because of its very low volatility (Rosenblatt et al. 1975b). There is the possibility that exposure to airborne diisopropyl methylphosphonate could occur if the compound was sorbed to soil and subsequently entrained by wind.

5.2.2 Water

Diisopropyl methylphosphonate was discharged in industrial effluent during the manufacture of the nerve agent GB (Sarin) during 1952-1957 at the RMA (EPA 1989; Robson 1977). Prior to 1956, the effluent from the production of Sarin was disposed of in five unlined surface ponds. Effluent percolated through the bottom of these ponds, entered the groundwater in a shallow alluvial aquifer, and resulted in groundwater contamination. In 1974, chemical analyses of the groundwater revealed the presence of diisopropyl methylphosphonate in a 73-km² area to the northwest of the arsenal and within 1.6 km (1 mile) of municipal water wells supplying the city of Brighton, Colorado (Robson 1977, 1981). The concentration of diisopropyl methylphosphonate in the groundwater ranged from 0.5 µg/L (the analytical detection limit) to 44,000 µg/L near one of the abandoned waste disposal ponds.

Groundwater samples collected over the last 10 years from monitoring and private water wells in the offpost area of RMA have provided data regarding the extent of diisopropyl methylphosphonate. The data indicate that diisopropyl methylphosphonate in the alluvial aquifer extends from the RMA northwest to the South Platte River. In the 1995 sampling event, diisopropyl methylphosphonate concentrations ranged from less than 0.392 µg/L, the detection limit, to just over 600 µg/L in this area. The highest reported concentrations were present upstream of the Peoria Street Treatment Plant. The lowest or non-detect concentrations are

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closer to the South Platte River. The treatment facility was installed in 1993 to intercept the contaminated groundwater north of RMA.

In 1996, chemical analyses of groundwater revealed the presence of DIMP in a 19.4 km² area located north and northwest of RMA, and within 11 km of South Adams County Water and Sanitation District (SACWSD) municipal water wells supplying the city of Commerce City (Harding Lawson Associates 1996).

DIMP contamination levels in the groundwater of Adams County around the RMA are decreasing due to treatment by the Army. The highest DIMP level in a well in 1997 was 1,500 µg/L. This well is in the vicinity of the offpost groundwater treatment system, operated by the Army, and will be intercepted and treated by the system. Downstream of the system, the highest diisopropyl methylphosphonate level was 660 µg/L in 1997. The Onpost Record of Decision in June 1996 provided that well owners with wells contaminated above 0.392 ppb could be connected to a municipal water supply. All well owners that accepted will be connected to the municipal supply by the summer of 1998. The Record of Decision also provides for wells to be connected in the future if diisopropyl methylphosphonate concentrations exceed values promulgated in the Colorado Basic Standards for Groundwater. Offpost surface water studies have not been conducted in 1998. In 1997, surface water near the RMA contained approximately less than the analytical reporting limit of 0.2 µg/L to 7.7 µg/L diisopropyl methylphosphonate.

5.2.3 Soil

No specific information was found on the releases of diisopropyl methylphosphonate to soil. However, diisopropyl methylphosphonate has been detected in soils at the RMA (Williams et al. 1989). Concentrations of diisopropyl methylphosphonate in five surface soil samples at the RMA ranged from <0.05 to 0.24 mg/kg (Williams et al. 1989). Concentrations of diisopropyl methylphosphonate in surface soil samples measured during the Remedial Investigation/Feasibility Study (RI/FS) at RMA ranged from less than the analytical limit of 0.114 mg/kg to 11 mg/kg (Ebasco Services 1991). The most recent sampling conducted in 1995 indicated the concentrations of diisopropyl methylphosphonate in the onpost surface soil samples were less than the analytical reporting limit of 0.342 mg/kg (D.P. Associates 1995).

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Diisopropyl methylphosphonate is slightly soluble in water (0.1-0.3 g/L at 25°) and has been demonstrated in laboratory studies to quickly diffuse between the surface microlayer into the water column after deposition as aerosols on fresh water (Van Voris et al. 1987). The solubility of diisopropyl methylphosphonate was 80 g/L (8%) and remained in solution even when the temperature was lowered to freezing (Bucci et al. 1997). In addition, there was no significant loss of diisopropyl methylphosphonate from the water column to the atmosphere, in either the presence or absence of a light wind over the water surface. Human exposure resulting from the vaporization of diisopropyl methylphosphonate from surface water is considered insignificant (EPA 1989).

Laboratory studies on the deposition of diisopropyl methylphosphonate to soils suggest that soil acts as a sink for this chemical (Van Voris et al. 1987). Deposition velocities of diisopropyl methylphosphonate for soil were approximately 0.87-1.2 cm/second when mass loading rates ranged from 300 to 3,000 $\mu\text{g}/\text{cm}^2$. Results of soil lysimeter studies indicate that the movement of diisopropyl methylphosphonate in soil occurs with irrigation water flow (O'Donovan and Woodward 1977a, 1977b). Moreover, the movement of diisopropyl methylphosphonate through various types of soil depends on the volume of irrigation water applied to their surfaces. Radioactive tracer experiments indicate that evaporation of diisopropyl methylphosphonate from dry soil is not significant (O'Donovan and Woodward 1977a, 1977b). Dry soils containing diisopropyl methylphosphonate retained over 95% of the initial radioactivity after approximately 250 hours of treatment. The moist soil samples retained somewhat less activity (approximately 78%).

Bioconcentration of diisopropyl methylphosphonate by various plants was studied in soil and in hydroponic cultures (O'Donovan and Woodward 1977a, 1977b). The hydroponic studies used corn, beans, radish, wheat, tomato, carrot, sugar beet, meadow fescue, rose, and juniper. The soil studies included carrot, wheat, alfalfa, sugar beet, and bean. The concentrations of diisopropyl methylphosphonate in the irrigation water used in the soil tests were 0, 1, 8, 20, 50, 100, 300, 500, 700, and 1,000 ppm. Hydroponic cultures contained 0, 1, 10, 100, and 1,000 ppm diisopropyl methylphosphonate. Results of the hydroponic studies demonstrated that bioconcentration occurred in most plants, with peak bioconcentration occurring primarily in the 1st month of growth. In general, the leaves of the plants displayed the highest concentration of diisopropyl methylphosphonate, which was up to 20 times greater than concentrations contained in the solutions. Other

plant parts typically did not concentrate diisopropyl methylphosphonate or did so in a very limited manner. Bioconcentration also occurred in plants when diisopropyl methylphosphonate was added to soil. When measured at 65 days after exposure, the concentration of diisopropyl methylphosphonate in plant tissues (in particular, the leaves) generally increased with increasing diisopropyl methylphosphonate concentrations in the irrigation solution.

5.3.2 Transformation and Degradation

5.3.2.1 Air

No information was found on the transformation of diisopropyl methylphosphonate in the atmosphere. Based on the results of environmental fate studies of diisopropyl methylphosphonate in distilled water and natural water, photolysis (either direct or indirect) is not important in the transformation of diisopropyl methylphosphonate in aquatic systems (Spanggard et al. 1979). The ultraviolet and infrared laser-induced photodegradation of diisopropyl methylphosphonate in both the vapor or liquid phase has been demonstrated (Radziemski 1981). Light hydrocarbon gases were the principal decomposition products. Hydrogen, carbon monoxide (CO), carbon dioxide (CO₂), and water were also detected.

5.3.2.2 Water

Diisopropyl methylphosphonate does not undergo direct or indirect photolysis in aquatic systems, as demonstrated by the stability of the compound in distilled water or in a natural water sample after 232 hours of reaction time with the mercury lamp filtered to exclude all wavelengths below 290 nm (Spanggard et al. 1979).

Biodegradation of diisopropyl methylphosphonate was not observed in acclimated cultures of bog water obtained from the RMA, even after the addition of extra carbon sources and an incubation period of up to 12 weeks (Spanggard et al. 1979). In addition, no biodegradation of diisopropyl methylphosphonate was observed in waters obtained from the Palo Alto sewage plant aeration tank or from a pond near Searsville Lake in Woodside, California.

5.3.2.3 Sediment and Soil

The biodegradation of diisopropyl methylphosphonate by microorganisms was studied in soil obtained from the RMA (Spanggard et al. 1979). Diisopropyl methylphosphonate was degraded to CO₂ by soil microorganisms, but the biodegradation was very slow, with only 13.4% of the original activity being evolved as ¹⁴CO₂ after 34 weeks of incubation. It was determined that soil biodegradation was not a function of the concentration of diisopropyl methylphosphonate. However, temperature can affect the soil biodegradation of diisopropyl methylphosphonate with transformation being very slow at 25° C (15-20%) and almost completely halted at 10° C (<0.1 %) (Spanggard et al. 1979). A half-life in excess of 2 years was predicted for diisopropyl methylphosphonate in soil. In another study of the microbial degradation of diisopropyl methylphosphonate in soil, ¹⁴C-diisopropyl methylphosphonate was converted to ¹⁴CO₂, to the extent of 6.4% and 6.0% in soils, uncontaminated and contaminated, respectively, obtained from the RMA (Williams et al. 1989). Results of a mass balance study revealed that the majority of the ¹⁴C-diisopropyl methylphosphonate was recovered as the undegraded parent compound.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

No information was found on levels monitored or estimated in the air. However, because of its very low volatility, diisopropyl methylphosphonate is unlikely to be an atmospheric contaminant (EPA 1989). A rate constant for diisopropyl methylphosphonate has not been determined.

5.4.2 Water

There are no measurements of the actual concentrations of diisopropyl methylphosphonate in groundwater at the RMA during the years of active production of the nerve gas Sarin (i.e., 1953-1957) (EPA 1989). The first actual measurements of the concentration of diisopropyl methylphosphonate in the groundwater on the arsenal and surrounding property to the north and west were made in 1974 (Robson 1981). The concentrations of diisopropyl methylphosphonate in the groundwater ranged from 0.5 µg/L (analytical detection limit) to as much as 44,000 µg/L near the abandoned waste disposal ponds. Diisopropyl methylphosphonate was discharged into a lined reservoir at the RMA in 1956 and was still present 20 years later in concentrations of about 400,000 µg/L (Robson 1977).

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During the most recent comprehensive groundwater sampling at RMA in 1995, diisopropyl methylphosphonate concentrations in groundwater were reported to range from less than 0.110 µg/L to 965 µg/L. The highest concentrations were reported near the areas of prior waste disposal. In 1997, offpost groundwater near the RMA contained less than the analytical reporting limit of 0.2 µg/L to 1,500 µg/L diisopropyl methylphosphonate (USGS 1998). In 1997, offpost surface water near the RMA contained less than the analytical reporting limit of 0.2 µg/L to 7.7 µg/L diisopropyl methylphosphonate.

In 1997, concentrations of diisopropyl methylphosphonate in onpost groundwater samples at the RMA ranged from less than the analytical reporting limit of 0.2 µg/L to 1,500 µg/L (USGS 1998). Concentrations of diisopropyl methylphosphonate in onpost surface water samples at the RMA ranged from less than the analytical reporting limit of 0.2 µg/L to 0.581 µg/L.

5.4.3 Sediment and Soil

The concentrations of diisopropyl methylphosphonate in 5 surface soil samples obtained at the RMA ranged from <0.05 to 0.24 mg/kg (Williams et al. 1989).

The most recent onpost surface soil sampling was conducted in 1995. Concentrations of diisopropyl methylphosphonate in surface soil samples measured in 1995 at RMA were less than the analytical reporting limit of 0.342 mg/kg, (D.P. Associates 1995). The most recent onpost subsurface soil sampling occurred in 1993. Concentrations of Diisopropyl methylphosphonate in 1993 at RMA ranged from less than the analytical reporting limit of 0.114 mg/kg to 0.864 mg/kg (Harding Lawson Associates 1994).

The most recent onpost sediment sampling occurred in 1990. All concentrations of diisopropyl methylphosphonate in sediment samples measured during the RI at RMA were less than the analytical reporting limits, which ranged from 0.05 mg/kg to 1.0 mg/kg (Ebasco Services Inc. 1992). Diisopropyl methylphosphonate has not been detected in sediment samples near the RMA. The most recent sampling for diisopropyl methylphosphonate occurred in 1990 and all the results were less than the analytical reporting limit of 1.0 mg/kg (Harding Lawson Associates 1992).

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5.4.4 Other Environmental Media

No information was located regarding concentrations of diisopropyl methylphosphonate in other environmental media.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Exposure of the general population to diisopropyl methylphosphonate is expected to be highly unlikely and to occur at extremely low levels, but data are insufficient for exposure estimates. Diisopropyl methylphosphonate has been detected in the groundwater and, to a lesser extent, in the surface water and soil at or near the RMA. If exposure of the general population to diisopropyl methylphosphonate were to occur, water would be the most likely source.

Although workers in facilities manufacturing diisopropyl methylphosphonate may have been exposed to the chemical during the active years of production, no occupational monitoring studies for diisopropyl methylphosphonate were located.

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Populations living near the RMA may be at risk of exposure to diisopropyl methylphosphonate. Individuals with diisopropyl methylphosphonate in their domestic wells are receiving their drinking water from alternative sources. According to the On-post Record of Decision (June 1996), well owners with wells contaminated above 0.392 µg/L of diisopropyl methylphosphonate could be connected to a municipal water supply.

5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of diisopropyl methylphosphonate is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of diisopropyl methylphosphonate.

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The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1 Identification of Data Needs

Physical and Chemical Properties. The physical and chemical properties of diisopropyl methylphosphonate are sufficiently well defined to allow assessment of its fate following release to the environment (EPA 1989; HSDB 1994; Robson 1981; Rosenblatt et al. 1975b). The solubility of diisopropyl methylphosphonate under various conditions is not well defined. No additional information is needed.

Production, import/Export, Use, Release, and Disposal. The risk for exposure of the general population to substantial levels of diisopropyl methylphosphonate is quite low. GB (Sarin) and diisopropyl methylphosphonate have not been produced in the United States since 1957, and there is no indication that U.S. production of these chemicals will resume (EPA 1989). No information exists regarding the import or export of diisopropyl methylphosphonate. Diisopropyl methylphosphonate has no known commercial uses, but has been used by the military as a simulant for chemical warfare agents (Van Voris et al. 1987).

Methods for disposing of diisopropyl methylphosphonate include microwave decomposition, ultraviolet and infrared laser-induced photodestruction, chemical oxidation coupled with ultraviolet radiation catalyzation, and adsorption using granular activated carbon (Bailin et al. 1975; Calgon 1977; Radziemski 1981; Zappi et al. 1990). However, no information is available regarding the amounts of diisopropyl methylphosphonate disposed of by each method.

Environmental Fate. The environmental fate of diisopropyl methylphosphonate has been investigated in several studies (O'Donovan and Woodward 1977a, B977b; Radziemski 1981; Robson 1977, 1981; Spanngord et al. 1979; Van Voris et al. 1987; Williams et al. 1989). This chemical is relatively unreactive and degrades slowly in environmental media. Diisopropyl methylphosphonate is a by-product of production at the RMA and is confined to the RMA and surrounding areas. Municipal water will be supplied to consenting drinking water well owners within the DIMP plume. Thus, potential exposure of the general

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population is low. Additional monitoring studies of the contaminated plumes will be useful to assess the transport of this chemical from the RMA.

Bioavailability from Environmental Media. Oral absorption of DIMP from water was found to be rapid in both the rats and minks (Bucci et al. 1992). Dermal absorption of DIMP in swine was reported to be between 3 and 7% through 7 days (Snodgrass and Metkler 1992). However, no studies were located regarding the bioavailability of diisopropyl methylphosphonate from other environmental media. Studies that investigate the bioavailability of diisopropyl methylphosphonate from soils would be useful in estimating exposure of persons who live near the RMA.

Food Chain Bioaccumulation. Bioconcentration of diisopropyl methylphosphonate occurs primarily in the leaves of plants (O'Donovan and Woodward 1977a, 1977b). However, DIMP also bioconcentrates in the edible root portions of radishes and carrots, and in the fruit of tomato plants at lower levels. Exposure may occur through the ingestion of fruits and vegetables that have been irrigated with DIMP contaminated water. Additional studies are needed to assess the potential for bioconcentration in plants. While it is possible that diisopropyl methylphosphonate may enter the food chain via animal feed, DIMP is rapidly changed to IMPA by animals that eat it. Therefore, it is unlikely that DIMP will be bioaccumulated in animals and be present further up the food chain.

Exposure Levels in Environmental Media. Monitoring data were not located for diisopropyl methylphosphonate in ambient air. This chemical has been detected in surface and groundwater receiving effluent from the RMA (ATSDR 1996). It has also been detected in soil at the RMA. Since this chemical is not expected to be prevalent in the environment and exposure of the general population is not expected to be of concern, monitoring of ambient environmental media does not appear to be required. However, monitoring of environmental media such as groundwater and soil in the vicinity of the RMA has been conducted to help determine the potential for exposure.

Exposure Levels in Humans. This information is necessary for assessing the need to conduct health studies on these populations. No occupational studies were located regarding exposure levels of diisopropyl methylphosphonate in humans. Workers conducting wildlife toxicity studies at the RMA reported effects that could be associated with exposure to diisopropyl methylphosphonate; however, the workers were also exposed to a number of other toxic chemicals. One study that attempted to determine levels of diisopropyl methylphosphonate or its metabolite IMPA in the urine of residents of communities adjacent to the RMA was

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unsuccessful because urine components may have reduced sensitivity to target analytes by producing interferences (ATSDR 1996). Additional monitoring of populations at the RMA or living in the vicinity of the RMA would help assess the effects of diisopropyl methylphosphonate on the general population.

Exposure Registries. No exposure registries for diisopropyl methylphosphonate were located. This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry.

5.7.2 On-going Studies

ATSDR, EPA, the state of Colorado, and Shelf Oil are developing a medical monitoring plan for the remediation of the RMA. Exactly what chemicals will be monitored has not yet been determined.